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20.5 Smart Materials Modeling

Manuel Laso

20.5.1 Introduction

The most salient feature of modeling work in the area of smart materials is its great diversity. Materials considered as smart span a staggeringly wide range. Smart materials run the gamut from the inorganic, monolithic crystalline materials, to the organic, polymeric, semicrystalline ones. Composites, polycrystalline materials, hydrated gels, magnetostrictive/ferromagnetic tagged composites, electrochromic materials, etc. to mention but a few, further expand the range of smart materials to be modeled. The complexity that arises from this great variety of material types is compounded with the wide range of interesting properties they display. Finally, the question of the time and the length of scales at which the modeling is to be implemented adds an extra level of complexity to the field: Even when applied to the very same material and the very same property, it frequently happens that different smart material modelers (i) look at the material at vastly different spatial or temporal scales, (ii) use completely unrelated modeling techniques, and (iii) even come to conclusions and modeling results, which can be unrelated for all practical purposes.

Polyvinylidene fluoride (PVDF) is often considered a smart material and provides a good illustration of this situation (Table 20.6):

(a) At the quantum chemical (QC) level, appreciable effort has been devoted to the determination of the electronic structure of PVDF via QC methods with a view to estimate the

TABLE 20.6 Representative Modeling Levels and Goals for Major Types of Smart Materials

Type of Material	Application	Modeling Level/Technique	Modeling Goal
Piezoelectric ceramic functional gradient	Actuators	Micromechanical CEs, composites (c), FE (d)	Electromechanical coupling Mechanical response
Piezoelectric ceramic-adaptive composites	Actuators Smart structures Smart rotors Structural damping Aerodynamic control	Micromechanical CEs, composites (c) FE (d)	Electromechanical coupling Mechanical response
Lithium insertion compounds	Smart batteries	QC (a)	Structure prediction Structure stability Energy diagrams Jahn–Teller distortion
Shape memory alloys	Mechanical Biomedical Microrobotics Microdevices Actuators	Micromechanical CEs, plasticity, composites (c) FE (d)	Shape memory effect Superelasticity Hysteresis
Smart polymers	Biomedical sensing Drug delivery Immobilization		
Electrostrictive ceramic	Ultrasonic transducers Actuators MEMS	FE (d)	Electromechanical coupling Mechanical response
Piezoelectric ceramic	Pressure sensors Accelerometers Gyroscope Resonators Filters	FE (d)	Electromechanical coupling Mechanical response
Smart coatings	Stress visualization	QC (a)	Mechanism of mechanoluminescence, band calculation
Magnetostrictive/ferromagnetic tagged composites	Composite cure and health monitoring	Micromechanical CEs (c) FE (d)	Nondestructive materials testing
Electrorheological fluids	Actuators Brakes Mechanical couplers	Colloid dynamics (c), Viscoelastic flow calculations (d)	Structure–property relationship Rheological CE Device design
Magnetorheological fluids	Shock absorbers Dampers Brakes	Colloid dynamics (c), Viscoelastic flow calculations (d)	Structure–property relationship Rheological CE Device design
Fiber sensors	Distributed sensors Bragg gratings Fabry–Perot sensor Optical signal processing Intelligent transportation Optical multiplexing	FE, analytical (d)	Optothermomechanical behavior
Organic gelators	Molecular recognition	QC (a) Atomistic MD and MC (b)	Crystal structure Molecular complementary
Gels/hydrogels	Drug delivery	Mesoscopic (c) Coarse-grained polymer MC (b)	Gel structure, transport behavior
Magnetostrictive materials	Transducers Sensors Actuators Motors Magnetometers	Micromechanical CEs (c) FE (d)	Magnetomechanical design

(*Continued*)

TABLE 20.6 Representative Modeling Levels and Goals for Major Types of Smart Materials **(continued)**

Type of Material	Application	Modeling Level/Technique	Modeling Goal
Giant magnetostrictive materials	Sensors	Micromechanical CEs (c)	Magnetomechanical design
	Actuators	FE (d)	
	Positioning devices		
	Dampers		
Smart ceramics	Intelligent synthesis	Chemical thermodynamics, chemical kinetics (d)	Reaction kinetics
			Reactor design and control
Smart paints	Vibrational sensor	Micromechanical CEs (c)	Electromechanical coupling
	Atmospheric sensor	FE (d)	Mechanical response
	Human skin mimicry		
Piezoelectric polymers	Structural active elements	Atomistic MD and MC (b)	Crystal structure prediction
	Strain sensors	Micromechanical CEs (c)	Electromechanical coupling
	Transducers	FE (d)	Polarization response
	Active and passive vibration control		
Functionally graded polymer blends	Damping	Micromechanical CEs (c)	Electromechanical coupling
	Artificial tissue	FE (d)	Polarization response
	Medical applications		
Smart perovskites	Nonvolatile memories electromechanical conversion fuel cells	QC (a) atomistic MD and MC (b)	Crystal structure Piezoelectricity Pyroelectricity Ionic conductivity
Smart skins	Sound control	Micromechanical CEs (c)	Electromechanical coupling
		FE (d)	
Thermoresponsive inorganic materials	Temperature-sensing responsive devices	QC (a) Atomistic MD and MC (b)	Crystal structure Phase transitions
Electrochromic materials	Smart windows	QC (a)	Band structure
	Architectural glazing		Transmittance
	Thermochromic devices		Ion conduction
	Thermotropic devices		

monomeric dipole. Very frequently, QC methods are applied to quite small fragments of the polymeric chains, sometimes even in vacuo. This applies especially to those most advanced and sophisticated QC methods available today.

(b) Somewhat similar work has also been performed at the atomistic level although the assignment of electronic distribution to individual atoms is not directly based on a fundamental QC approach. At this level, the description of PVDF is based on a classical picture of atoms as sites interacting via an empirical force field. Typical modeling goals at this level are the correct calculation of crystalline polymorphs, and an estimation of piezoelectric, dielectric, and elastic properties via molecular dynamics (MD) and Monte Carlo (MC) methods. Prediction of electric properties is frequently limited by the use of partial charges to describe the spatial electron distribution.

(c) At the mesoscopic level, questions such as the stacking of folded PVDF lamellae, the prediction of semicrystalline morphology, and the prediction of piezoelectric moduli based on homogenization are addressed.

(d) At the macroscopic level, modeling PVDF often refers to the simulation and design of a particular geometry or device based on a purely continuum-mechanical description of the material via partial differential equations. All smart material information is condensed in a few macroscopic parameters, like piezoelectric moduli, elastic compliances, etc. At this level, modeling goes well beyond the material itself and is intimately linked to the design of a specific device for a specific function.

In spite of the general propensity to consider one's own specialty field as slightly more central and momentous than others fields, or to consider, say, quantum mechanics more fundamental than finite elements (FE), scientists and engineers working at any of the four levels just described are justly and equally entitled to claiming their work as smart materials modeling. For some specific materials, it also happens that modeling efforts at the different levels develop more or less independently of each other, with little if any communication among them. This state of affairs is easily detected by the corresponding sets of cited literature being often disjointed or having minimal overlap.

tionships between generalized fluxes and generalized forces (spatial gradients, driving forces) in the spirit of linear irreversible thermodynamics. In other cases, CEs are formulated as differential, integral, or integral differential equations. Material properties appear as characteristic magnitudes relating several fields, e.g., a Newtonian viscosity relates the rate of strain tensor and the stress tensor.

In the general case, only the complete set of equations that appear in the three blocks is solvable. Its solution consists of the macroscopic fields and their time dependence, possibly including an asymptotic approach to a steady state.

In the PVDF example, a set of stress, strain, electric field, and electric displacement fields (i.e., their values at every point in space and their variation in time) can be obtained by writing down and solving a set of equations in Blocks 1 to 3. Since the previous discussion is based on a purely macroscopic level of description (level (d) in the list in Section 20.5.1), it would be perfectly adequate and self-contained if the modeling goal were to achieve a quantitative description of the electric polarization of a PVDF piezoelectric of a given equilibrium shape when subjected to a given stress. In order to perform modeling at this macroscopic level, elastic compliances, dielectric permittivities, and piezoelectric moduli must be available, coming either from an experiment or possibly from a lower level modeling technique.

Modeling at levels (a), (b), and (c) are however quite different: now the goal is not to compute the solution of a complex (heterogeneous) problem for a particular material geometry. It is rather the prediction under very simple (e.g., homogeneous) conditions and starting from some basic principles (the meaning of basic being now level-dependent) of some or all of the physical, chemical, and thermodynamic properties that appear in the EOS and in the CEs, so that the modeler at level (d) can take them as input. In this sense, one of the goals of levels (a), (b), and (c) is to focus on Blocks 2 and, above all, 3 and pass on the information, which is required at level (d) to deal with the complete set of Blocks 1, 2, and 3.

It is however also true that information passing takes place across these three first levels (a), (b), and (c):

- Some of the parameters appearing in the force field for classical MD modeling (level b) of PVDF may come from semiempirical or ab initio QC calculations (level a).
- Atomistically computed crystal and amorphous matrix compliances via Parrinello–Rahman MD (level b) can be used to predict overall PVDF elastic compliance via homogenization methods borrowed from the theory of composites (level c).

* As a side comment, EOS and CEs can be detected by their carrying a surname: On the one hand, conservation laws are universal and one would be hard pressed to associate a person's name with their discovery. However, many EOS and all CEs are only plausible postulates but by no means universal laws. The inventor of such a plausible postulate seems to be naturally entitled to append his/her name to the corresponding equation, hence Fourier's, Fick's, Newton's, and Ohm's laws for heat, mass, momentum, and electric charge transport, respectively.

Thus, what is an output at a given level represents a necessary input at the next higher level. In this sense, it is now possible to assign modelers (a), (b), and (c) to the EOS and CE blocks. Modeler (d) must include all three blocks in the modeling work.

The reader looking for an entry point in the field of modeling smart materials is urged to first devote some effort to carefully consider at what level or levels his or her modeling should take place. A good deal of frustration can be avoided by a judicious choice of the correct description level.

It should also be mentioned that multiscale modeling methods exist and are gaining increasing popularity. Such hierarchical modeling techniques are undergoing rapid development and are bound to have a significant impact on the modeling of smart materials in the near future. The key idea behind multiscale modeling is to link in a single modeling approach two or more techniques residing at differential time/length scales ((a) through (d) above). As a prototypical example, the possibility of linking QC (density functional theory [DFT], actually) with classical MD and FE modeling techniques in a single calculation [1] has already been demonstrated for crack propagation in Si.

20.5.3 Informal Classification of Modeling Techniques for Smart Materials

is a fairly comprehensive list of materials considered as smart together with their applications and suitable modeling techniques. As expected, modeling goals range from the very microscopic, low-level ones (band calculations, crystal structure prediction, etc.) to the completely phenomenological and macroscopic (design of transducers, actuators, etc.). Furthermore, at the largest spatial scales (level d above) the modeling of the material itself, i.e., its equations of state and CEs, blends into the overall problem formulation, i.e., the design of a smart structure. Since the goal of the present chapter is the modeling of smart materials, it would be desirable to draw as clear a dividing line as possible in order to separate the modeling of the material itself from that of the structure.

This separation is closely linked to the idea of homogeneity: Except for materials whose smart function depends on being intrinsically graded, the modeling of the material itself is best addressed in a homogeneous setting. It is also possible that the goal of the modeling is precisely the determination of average (homogenized) properties. Unfortunately, the line that separates modeling a material from modeling a structure is often blurred.

We can group the modeling methodologies that appear in a few rather well-defined families. The following list refers to some of the most basic literature in each area. The list and the references at the end of the chapter are by no means exhaustive, but they represent useful entry points:

- Quantum chemistry methods [2]
  - Ab initio QC, including Car–Parrinello MD [3]
  - Semiempirical [4]
- Classical atomistic methods

- MD [5]
- MC and hybrid MC [6]

- Mesoscopic methods
  - Brownian/stochastic dynamics [7]
  - Lattice Boltzmann [8]
- Coarse-graining methods:
  - Micromechanical modeling [9]
  - Composite theory [10]
- Discrete techniques for partial differential equations:
  - Galerkin and its variants (Petrov–Galerkin, generalized Galerkin) [11]
  - Collocation [12]
  - Meshless methods [13]
- Nonequilibrium thermodynamics
  - Linear irreversible thermodynamics [14]
  - Generic [15]

As a general introduction to the field of smart materials, and not only their modeling, Ref. [16] is highly recommended.

20.5.4 Conclusion

The great diversity and the range of smart materials make it very difficult to draw general conclusions about their modeling. Only a few general guidelines can be suggested:

- Strive for a clear separation between modeling a smart material, and modeling a smart device or structure. Be aware that in some cases, this separation is not possible.
- Prior to any modeling work, carefully consider the general modeling situation depicted. Decide at which levels the smart material is to be modeled.
- Clearly distinguish equilibrium and nonequilibrium modeling goals.
- Clearly distinguish between homogeneous and nonhomogeneous situations.
- If multilevel modeling is involved, pay extra attention to consistent coarse-graining and thermodynamic admissibility [15].

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20.6 On the Microstructural Mechanisms of Shape Memory Effects

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Shape memory alloys (SMAs) have the unique ability to recover their exact original shape even after large macroscopic displacements. Typical elastic–plastic materials begin to permanently deform at strains less than 1%, while in SMAs, this can be as high as 8% [1]. The "magic" behind this property is rooted in the martensitic phase transformation that is driven by either a change in temperature or a change in stress [2,3]. While having the existence of this solid-state transformation is necessary for shape memory effects (SME) to occur, it is not a sufficient condition (martensitic transformations were first seen in steels, where SMEs are not observed [4].). The property of thermoelasticity is critical in determining whether a material that undergoes this type of phase transformation will exhibit shape memory. It is necessary to discuss the microscopic details of this reaction to develop a systematic understanding of the macroscopic effects of thermal shape memory (commonly called shape memory) and mechanical shape memory (commonly called superelasticity) that are of interest to engineers developing practical applications. The more common description of SMAs discuss these two effects separately, giving the impression that they are only arbitrarily related and just happen to occur in the same material. In the second half of this chapter, we will show that these two macroscopic effects lie on a